Concept for a Hydrometallurgical Processing of a Copper-Cobalt-Nickel Alloy Made from Manganese Nodules

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The processing of manganese nodules for the production of raw materials has been a subject of research for many decades. The nodules contain many valuable metals like copper, cobalt and nickel. In recent years, the German Federal Institute for Geoscience and Natural Resources developed a process for the processing of manganese nodules based on a combined pyro- and a hydrometallurgical route. Clausthal University of Technology was assigned to develop the hydrometallurgical process for the treatment of a FeNiCuCo alloy. The developed process consists of pressurized sulfuric acid leaching with the suppression of hydrogen gas formation, precipitation and solvent extraction.

Keywords: Alloy leaching, Hydrometallurgy, Manganese nodules, Precipitation, Solvent extraction

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1 Introduction

Manganese nodules are found on sedimented seafloor in the deep sea all around the world. They consist of thin layers of manganese oxides and iron oxyhydroxides that form around a nucleus. In the nodule, a variety of different elements can be enriched. Most nodules have a diameter between 1 and 10 cm and a spherical to discoidal shape. The growth rate of the manganese nodules may differ through time and deposit and ranges between a few mm to a few cm per one million years. The nodules contain many elements of economic interest especially copper, nickel and cobalt, but also traces of zinc, molybdenum, vanadium, titanium, zirconium, gold, platinum, palladium and rare earth elements [1, 2].

Since the 1960s, the nodules have gained more and more interest as a source of nonferrous metals and many attempts were undertaken to process them. Mineral processing techniques like flotation have not been successful due to the extremely fine intergrowth of the phases. The size of the metal phases within the manganese nodules ranges between 0.01 to 0.05 µm, a range in which mineral processing techniques are not applicable for physical and economic reasons. Therefore, different hydrometallurgical and pyrometallurgical processes have been developed, some of them up to pilot scale [3].

The processes developed in the past can be divided into pyrometallurgical processes based on smelting, chlorination, vaporizing and segregation, and hydrometallurgical processes based on acid leaching, ammonia leaching and leaching with reducing reagents [3]. In the pyrometallurgical processes, the high water content of the manganese nodules is a big disadvantage because of the high energy consumption for drying [3]. The main disadvantage of the direct hydrometallurgical treatment of the manganese nodules is the high consumption of reagents because no preenrichment takes place [4]. A typical composition of manganese nodules is given in Tab. 1.

In 1976, Sridhar et al. introduced a pyrometallurgical process combined with hydrometallurgical extraction developed by the former International Nickel Company (Inco). The aim of this process is to reduce the mass that has to be leached in the hydrometallurgical process. [5]

The Inco process, shown in Fig. 1, starts with a combined drying and reduction step, which takes place at 1000 °C in a rotary kiln. After this step, the nodules are smelted between 1380–1420 °C and separated in a manganiferous slag and an alloy consisting of iron, nickel, copper and cobalt. The alloy is further processed by a converting process to obtain a sulfidic matte, which is then treated hydrometallurgically. Sridhar et al. suggested pressure oxidation leaching (POX). [5]

In recent years, the German Federal Institute for Geoscience and Natural Resources (BGR) together with RWTH

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Table 1. Average chemical composition of dried manganese nodules from the German license area in the Clarion-Clipperton Fracture Zone (CCZ).

Element	Value
Co [%]	0.16
Cu [%]	1.17
Mn [%]	31.2
Ni [%]	1.36
Other [%]	66.11

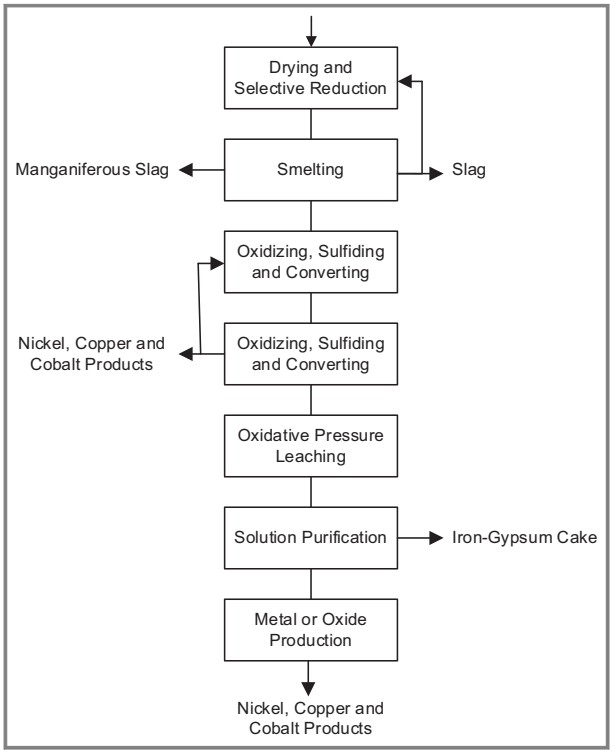

Figure 1. Flowchart of the Inco process [5].

Aachen University improved the Inco process, with the aim to bring the process to industrial scale. The RWTH Aachen optimized the pyrometallurgical approach in order to develop a zero-waste process in which all components of the nodules can be utilized. Therefore, besides optimization of the smelting a second smelting step was added to process the manganese-rich slag further. In this second smelting, high carbon ferromanganese is produced, which can be used in the production of manganese steel. The slag is depleted of the heavy metal content and can be used in the construction industry. In contrast to the work of Sridhar et al., the FeNiCoCu alloy undergoes no converting to a sulfidic matte but is directly processed hydrometallurgically. Therefore, the pyrometallurgical process has three main products: the FeNiCoCu alloy, which is further processed by hydrometallurgical treatment, ferromanganese, and the slag as a mineral byproduct. [4, 6]

The Institute of Mineral and Waste Processing, Waste Disposal and Geomechanics (IFAD) at the Clausthal University of Technology was assigned by the BGR to develop a concept of a hydrometallurgical process for the treatment of the FeNiCuCo alloy. Based on literature research and supporting experiments, the focus was to develop an economically feasible process. The sample materials, i.e., a Fe-rich metal alloy, were provided by the RWTH Aachen and produced from manganese nodules from the German license area of the Clarion-Clipperton-Zone (CCZ) in the Pacific Ocean.

2 Theory

The alloy produced by the pyrometallurgical process contains mainly the valuable metals copper, cobalt and nickel. Options for further processing for alloys are POX, ammonia leaching and anodically dissolving in acidic electrolytes [7].

For the investigation of this work, a POX process was chosen as it has been proven successful for similar materials at industrial scale, i.e., at the Chambishi Metals cobalt plant in Zambia [8]. The alloy can be leached with sulfuric acid. Typical conditions are temperatures between 135–150 °C and oxygen pressures between 8–10 bar. Due to the ignoble metals present in the alloy, hydrogen formation can take place during leaching, which can lead to serious safety hazards. The reaction equations for the direct leaching of the metal alloy with sulfuric acid are shown in Eqs. (1)–(4). The leaching of copper does not lead to the formation of hydrogen gas [8].

$$\mathrm{Co(s) + H_2SO_4 \rightarrow CoSO_4(aq) + H_2(g)} \quad (1)$$

$$\mathrm{Fe(s) + H_2SO_4 \rightarrow FeSO_4(aq) + H_2(g)} \quad (2)$$

$$\mathrm{Ni(s) + H_2SO_4 \rightarrow NiSO_4(aq) + H_2(g)} \quad (3)$$

$$\mathrm{Cu(s) + 0.5O_2 + H_2SO_4 \rightarrow CuSO_4(aq) + H_2O(l)} \quad (4)$$

To prevent the formation of hydrogen, copper sulfate is added to the leaching solution. In this case, cementation of the copper through the less noble metals takes place (Eqs. (5)–(7)). However, the cemented copper is also leached by sulfuric acid according to Eq. (4). [8]

$$\mathrm{Co(s) + Cu_2SO_4 \rightarrow CoSO_4(aq) + Cu(s)} \quad (5)$$

$$\mathrm{Fe(s) + Cu_2SO_4 \rightarrow FeSO_4(aq) + Cu(s)} \quad (6)$$

$$\mathrm{Ni(s) + Cu_2SO_4 \rightarrow NiSO_4(aq) + Cu(s)} \quad (7)$$

After leaching, the purification of the pregnant leach solution takes place. The further processing of the leaching

solution is done based on established processes. Besides the target element copper, cobalt and nickel, the alloy also contains a significant amount of iron. Iron is typically removed prior to the separation and purification of the nonferrous metals by precipitation in order to avoid interference with the solvent extraction processes. Industrially established precipitation methods are hematite, goethite and jarosite precipitation. A similar approach is used by Nickelhütte Aue for the processing of their intermediates, which is shown exemplarily in Fig. 2 [9].

The precipitation of hematite takes place at 200 °C and can be performed in the same process step as the leaching. The advantage of iron precipitation in the form of hematite is the small volume of the product, leading to less solid waste. The greatest disadvantage is the high residual iron content in the solution, which makes a second precipitation step necessary. Eqs. (8) and (9) show the reactions for the precipitation. In the first step, iron(II) is oxidized by oxygen to iron(III). In the second step the iron is precipitated as hematite. [10, 11]

$$2FeSO_4(aq) + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3(aq) + H_2O \quad (8)$$

$$Fe_2(SO_4)_3(aq) + 3H_2O \rightarrow Fe_2O_3(s) + 3H_2SO_4 \quad (9)$$

The precipitation reaction of goethite is shown in Eq. (10). It takes place at temperatures between 80–95 °C and pH values above 2. In comparison, goethite precipitation leaves very low residual contents of iron in the solution. In the case of the manganese nodule alloy, the precipitation of goethite could lead to a loss of the target elements. A co-precipitation of cobalt and nickel can take place because both elements can substitute iron in goethite. Especially nickel can also adsorb on the surface of goethite, and thus, will also be removed partly from the solution [12–14].

$$2Fe^{2+} + H_2O_2 + 2H_2O \rightarrow 2FeOOH + 4H^+ \quad (10)$$

The precipitation of iron as jarosite is a standard operation widely used in the production of zinc. Eq. (11) shows the reaction of the precipitation. It can be carried out at temperatures between 90–100 °C and a pH of 1.5 by adding sodium, potassium or ammonium ions to the solution [15].

$$3Fe_2(SO_4)_3 + 2NaOH + 10H_2O \rightarrow 2NaFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad (11)$$

After removal of iron, the target elements can be won from the solution. Especially for copper and cobalt, solvent extractions are already established unit operations. For the extraction of copper, oximes are the most common extractants. For the extraction of cobalt from sulfate solutions, phosphonic acids are used. In this work, the usage of solvent extraction for copper and cobalt is investigated. [10, 16, 17]

Depending on the desired products, the metals can be recovered from solution by electrolysis, crystallization and precipitation.

For nickel, the precipitation as nickel carbonate can be an alternative to a solvent extraction process. The nickel in the leaching liquor is precipitated as basic nickel carbonate. The precipitation is conducted at elevated temperatures above 80 °C and a pH above 7 by adding sodium carbonate to the solution as shown in Eq. (12). [18]

$$4Ni^{2+} + CO_3{}^{2-} + 6OH^- + 4H_2O \rightarrow Ni_4CO_3(OH)_6(H_2O)_4 \quad (12)$$

3 Materials and Methods

3.1 Analysis

For the digestion of the sample material, an aqua regia digestion is carried out. The chemical analysis is then conducted by inductively coupled plasma optical emission spectrometry (ICP-OES) with an Agilent 5100 ICP-OES. The sample solutions of the experiments are also analyzed by ICP-OES.

The X-ray diffraction analysis (XRD) for the precipitation products is carried out with a Philips X'Pert Powder.

3.2 Sample Material

The RWTH Aachen provided different samples of the alloy. The first sample (sample 1) is derived directly from the smelter, while later samples (sample 2) underwent a converting process to lower the iron content. Due to the ongoing optimization and scale-up of the process, the current alloy does not represent the final quality. In the future, lower iron contents can be expected. Tab. 2 provides the chemical composition of two alloy samples used during this study.

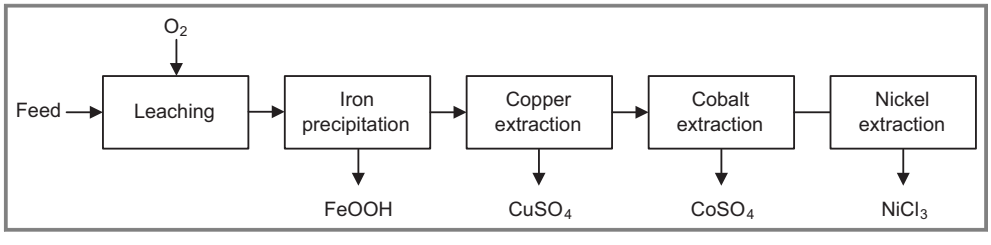

Figure 2. Flowchart of the CuCoNi separation process of Nickelhütte Aue [9].

Table 2. Chemical composition of two alloy samples measured with ICP-OES.

	Sample 1	Sample 2
Co [%]	1.75	2.92
Cu [%]	12.80	23.7
Fe [%]	56.80	38.8
Mn [%]	3.60	0.0038
Ni [%]	16.38	32.1
Other [%]	8.67	2.44

The leaching experiments are conducted with these materials. Due to the wide particle size distribution of the alloy and to shorten the leaching time, the sample has been classified. The fraction 0.5 to 0.8 mm is used for the leaching experiments. However, due to the classification, a generic solution has to be used for further experiments due to the limited amount of alloy in the target grain size available.

The composition of the generic solutions produced by the dissolution of the respective sulfates is shown in Tab. 3. The generic solution based on sample 2 contains no copper or iron because it was only used for experiments to separate cobalt, nickel and manganese. In all experiments, chemicals of analytical quality are used.

Table 3. Metal contents of the generic solutions analyzed with ICP-OES.

	Sample 1	Sample 2
Co [mg L^{-1}]	3651	7870
Cu [mg L^{-1}]	27 431	–
Fe [mg L^{-1}]	9047	–
Mn [mg L^{-1}]	7405	10.34
Ni [mg L^{-1}]	33 481	87 800

3.3 Experiments

3.3.1 Leaching and Hematite Precipitation

For the leaching experiments, an autoclave system type polyclave from Büchi AG is used. It is equipped with a jacketed 3-L pressure vessel made out of alloy 2.4602. It is stirred with a speed of 500 rpm. The temperature is controlled by a thermostat. The pressure is controlled manually.

The following parameters are used for the leaching: 1.5 sulfuric acid excess, 2–3 copper sulfate excess, temperature = 150 °C, oxygen pressure = 10 bar, concentration of solids = 25–45 g L^{-1}. The leaching time is 6 h.

In the hematite precipitation experiment, the leaching of the alloy is performed with modified parameters. The temperature is gradually raised to 200 °C and the leaching time raised to 8 h, while all other parameters stay the same.

3.3.2 Non-pressurized Precipitation

The precipitation experiments are carried out in glass beakers. The temperature is controlled by heating plates with PID controllers.

3.3.3 Solvent Extraction

For solvent extraction, separating funnels are used. The mixing takes place on a shaking table with a frequency of 250 min^{-1}. The ratio between organic phase and aqueous phase is 1:1, the total volume of the aqueous and organic phase is 100 mL. The organic phase consists of the extraction agent and diluent with a ratio of 1:1, here Exxsol D100. In all experiments, the contact time is 5 min.

4 Results and Discussion

In the following, the results of the experimental work are presented and discussed. The aim is to develop an economic process route for the hydrometallurgical treatment of the FeNiCuCo alloy provided by RWTH Aachen. For the precipitation of iron, only the results that are important for the conception of the process are presented in this paper. Due to the expected reduction of the iron content in the alloy the designing of the final precipitation is an ongoing task that can only be completed when the final composition is known.

4.1 Leaching and Hematite Precipitation

In a first experiment, the FeNiCuCo alloy provided by RWTH Aachen was leached with copper sulfate according to Eqs.(4)–(7). The high copper sulfate excess was chosen to prevent hydrogen gas formation. The solid/liquid ratio is limited by the solubility of copper sulfate, leading to a low ratio.

The results showed complete dissolution of the alloy within 6 h. An oxyhydrogen test showed no explosive atmosphere in the autoclave. In a second experiment, leaching with simultaneous precipitation of hematite is investigated, but no satisfactory results achieved. Although the alloy is completely leached, only about 10 % of the iron is removed from the solution within the given time of 8 h. Due to the high corrosion rate at elevated temperature in the autoclave, no further experiments were conducted. The compostions of the solutions from both experiments are shown in Tab. 4. The reason for the partly precipitation might be the grain size of the alloy which leads to long leaching times.

Table 4. Metal contents of the leaching liqueurs.

Experiment	Material	Co [g L^{-1}]	Cu [g L^{-1}]	Fe [g L^{-1}]	Mn [mg L^{-1}]	Ni [g L^{-1}]
Only leaching	sample 1	0.43	70.47	14.25	850	4.03
With precipitation	sample 2	1.32	79.42	15.90	2.7	17.40

4.2 Non-pressurized Precipitation of Iron

Besides the precipitation as hematite, two other routes of iron precipitation are suggested: precipitation as goethite and jarosite.

In the experiments for the goethite precipitation it has not been possible to precipitate only iron while copper is present in the solution. While only 21 % of the iron is removed, also 38 % of the copper is precipitated as copper oxide. Fig. 3 shows the XRD spectrum of the precipitation product. Copper oxide is the only crystalline component that could be measured. Precipitation of cobalt and nickel could not be observed. This means that the goethite precipitation must take place after the solvent extraction straight after the copper extraction. Final experiments on the goethite precipitation are shifted until the final composition of the alloy is known and more original material is available.

The precipitation of jarosite can be an option if the precipitation of hematite and goethite will show disadvantages in future experiments with material in the final composition. Because hematite and goethite are favored at the moment because of the lower volume of the product (hematite) and lower residue iron concertation (goethite), the experiments for jarosite are deferred to a later stage.

4.3 Solvent Extraction

After the removal of iron, the selective extraction of the target elements is investigated. The first element to extract by solvent extraction is copper. For the solvent extraction of copper, different selective extraction agents are available. Two agents were tested, LIX-860-IC and LIX-860N-IC, both produced by BASF. As shown in Fig. 4, LIX-860-IC has a high selectivity and high recovery for copper for the investigated pH range. No significant differences are observed for LIX-860N-IC. The usage of solvent extraction for the copper separation has the advantage of a partial recirculation of the stripped copper sulfate solution to the leaching stage.

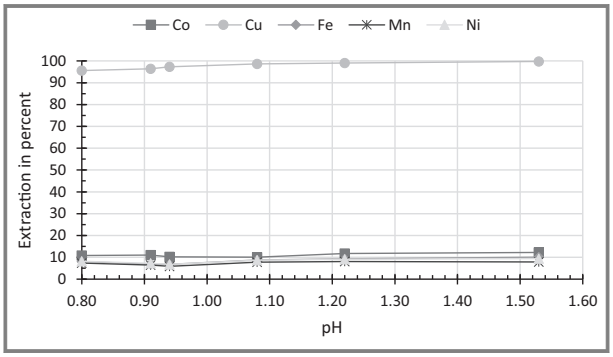

Figure 4. Results for the extraction of copper with LIX-860-IC.

For further processing, two options for the extraction of cobalt were considered: solvent extraction of the cobalt with Cyanex 301 or Cyanex 272 both produced by Solvay. Flowcharts for both ways are shown in Fig. 5. Cyanex 301 has the advantage that it has a high selectivity over manganese but no selectivity over nickel [19]. That means that in a first step cobalt and nickel are extracted together by Cyanex 301 and after stripping cobalt and nickel must be separated in a second step. However, Cyanex 301 is highly sensitive to oxidization and metal poisoning, therefore, and due to the low manganese content after the converting step, (see Tab. 2) the use of Cyanex 301 was not investigated.

The general order of selectivity for Cyanex 272 is Co/Mn > Ni. Therefore, manganese will be enriched in the organic phase, if it is not removed prior to extraction. An option to remove manganese selectively from the solution by precipitation is a precipitation as MnO_2. The precipitate can be recycled to the smelter. [17]

Alternatively, cobalt and manganese can be extracted together. Cobalt can then be stripped selec-

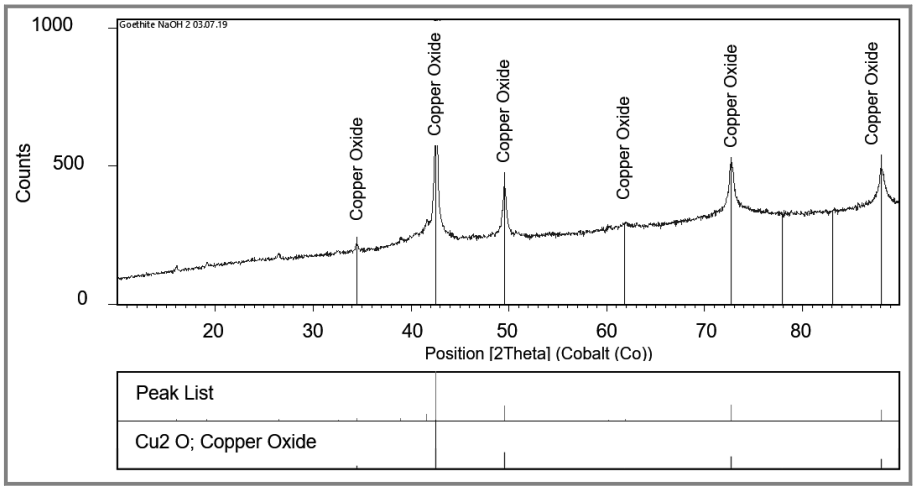

Figure 3. Results for the XRD analysis of precipitation product of the goethite experiments.

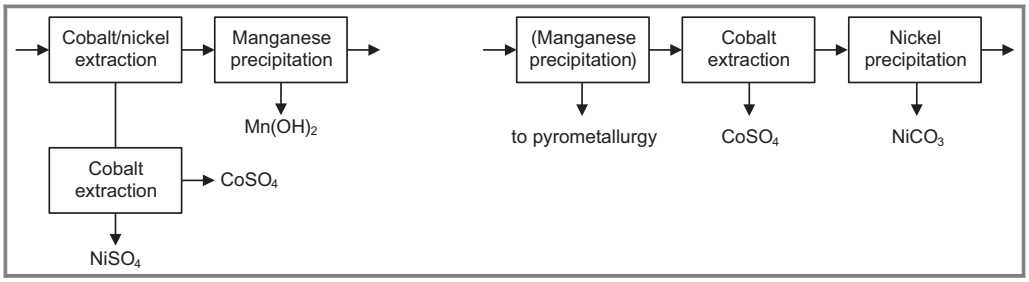

Figure 5. Flowcharts for the two process routes to extract cobalt. Left: Cyanex 301, right: Cyanex 272.

tively, leaving the manganese in the organic phase. Due to the continuous enrichment, manganese has to be stripped in a second stripping to avoid contamination of the cobalt product.

To examine the feasibility of the extraction with Cyanex 272, a generic solution containing cobalt and nickel was used. The results are shown in Fig. 6. As expected, the extraction of cobalt increases with the pH value. At a pH of around 5, a cobalt extraction of 80 % can be achieved with an extraction of nickel below 10 %, demonstrating very high selectivity.

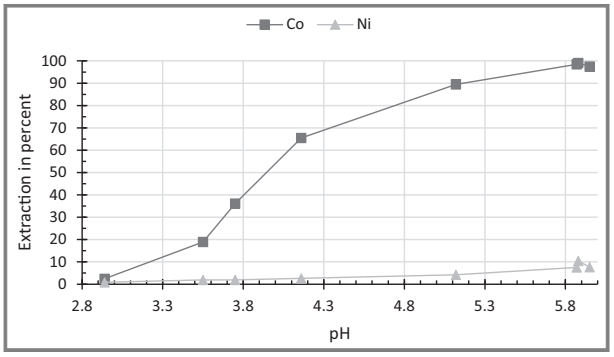

Figure 6. Results for the extraction of cobalt by Cyanex 272 from a generic solution with cobalt and nickel, only.

To investigate the effect of manganese, the same experiment was conducted with a generic solution containing cobalt, nickel and manganese. The results are shown in Fig. 7. It can be seen that the extractive behavior of manganese and cobalt is quite similar, although, manganese is extracted preferably. Certainly, the concentration of manganese is low enough that is has no effect on cobalt extraction, allowing for a selective stripping of cobalt as described above.

After extraction of cobalt, nickel can be precipitated for example as basic nickel carbonate, a typical intermediate in nickel processing. Alternatively, direct refining by a further solvent extraction process is possible. Compared to solvent extraction, the precipitation of the nickel requires much lower investment and operational costs.

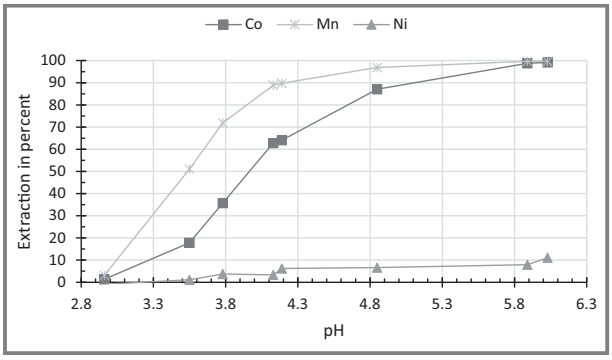

Figure 7. Results for the extraction of cobalt by Cyanex 272 from a generic solution with cobalt nickel and manganese.

5 Proposed Process and Conclusion

The treatment of manganese noodles with a combined and pyrometallurgical process seems to be a promising concept for the recovery of the valuable metals, copper, cobalt and nickel. In the presented paper, a hydrometallurgical concept of the FeNiCuCo alloy has been developed. Fig. 8 shows the complete flowchart for the suggested treatment.

In the first step, the leaching is carried out in an autoclave under the addition of copper sulfate to prevent the formation of hydrogen gas. After the leaching, the copper is extracted by solvent extraction. After the stripping, the sulfate solution can be partly recycled as leaching agent, while metallic copper is won by electrowinning. Next, the iron has to be removed from the process stream before further treatment. Goethite precipitation seems to be the best option for iron removal due to the low residual concentration. During the goethite precipitation, co-precipitation of cobalt and nickel are possible. A loss of these metals can be avoided by recycling of the precipitate to the smelting operations. This has also the advantage that no iron product has to be deposited in the hydrometallurgical process, thus, fulfilling the proposed zero-waste concept. However, a more detailed investigation of the iron precipitation is necessary to finally evaluate this step.

After the removal of iron, the solvent extraction of cobalt can take place. Before cobalt extraction can be realized, a manganese precipitation step might be needed if manganese is still present in the metal alloy in a significant concentra-

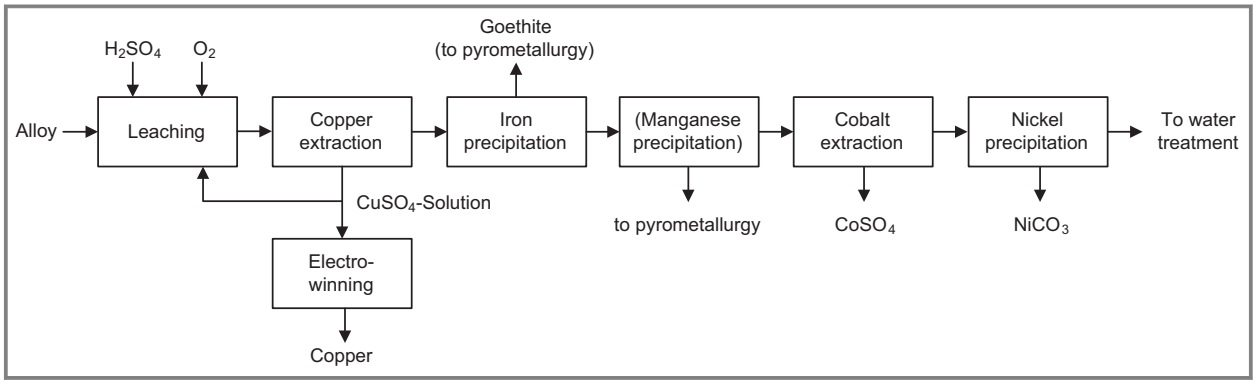

Figure 8. Proposed flowchart for the processing of the manganese nodule alloy.

tion. The cobalt solvent extraction can be done with Cyanex 272, leading to a high-quality cobalt product. The remaining nickel in the process solution can be precipitated as nickel carbonate. All steps of the proposed hydrometallurgical treatment of the manganese nodule alloy are approved at an industrial scale or are industrial standard operations.

In conclusion, the processing of manganese nodules in a combined process with a pyrometallurgical and a hydrometallurgical process is possible. Due to the combination of pyro- and hydrometallurgy, a zero-waste process can be realized by recycling waste stream from the hydrometallurgy to the pyrometallurgical process.

Before the process can be realized in the industrial scale, many parameters have to be investigated in detail. For example, the chosen parameters used for the leaching in the experiments are not economically feasible due to the low liquid/solid ratio and the requirement of a more elaborate solvent extraction process, which would lead to high investment and operational costs. Therefore, an optimization of the leaching must take place or alternatives like a pyrometallurgical conversion of the alloy to a sulfidic matte, what is also discussed in literature by Sridhar et al. [5], should be tested. In addition, the grain size of the alloy must be reduced by the use of an atomizer. This would lead to much shorter leaching times and might make the precipitation of hematite possible in a reasonable time.

The precipitation of the iron must be investigated in detail in the future. Most of the experiments are deferred to a state where the final composition of the alloy is known, and the experiments can be conducted with original material instead of generic solutions.

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Abbreviations

BGR	German Federal Institute for Geoscience and Natural Resources
ICP-OES	inductively coupled plasma optical emission spectrometry
IFAD	Institute of Mineral and Waste Processing, Waste Disposal and Geomechanics
POX	pressure oxidation leaching
XRD	X-ray diffraction analysis

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